Nanocasting – Introducing Secondary Supports into Metal-Organic Frameworks to Increase their Stability

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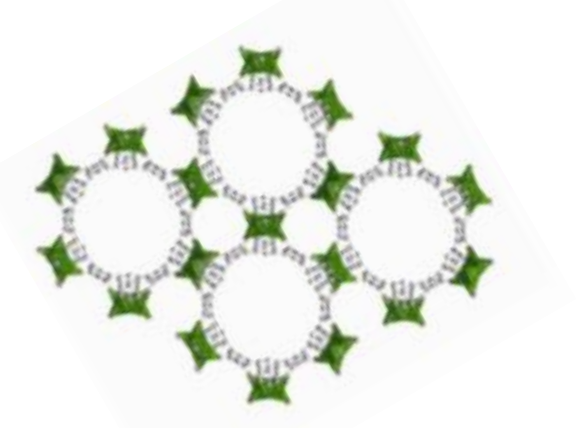
Abstract

Nanocasting[1] is a technique of adding a secondary support or "scaffold" to metal-organic frameworks (MOFs) with the aim to enhance the stability of catalytic sites in the MOF. MOFs of interest for this study include NU-1000[2], NU-901 and aluminum-cobalt modified[3] NU-1000 with oxozirconium clusters as nodes, linked together by organic groups to produce a porous framework. For the nanocasting process, silica was used to coat the inner surface of these MOFs in order to keep cluster sites separated at high temperature (~500 °C). After nanocasting, the oxozirconium nodes and associated catalytic properties were maintained even after the materials underwent treatment at high temperatures, in contrast to MOFs that had not undergone nanocasting treatment so that oxozirconium nodes sintered to form bulk zirconia at high temperatures. In order to verify the compatibility of nanocasting with other MOFs, MOFs having different metal clusters were also examined. These include DUT-9[4] (Ni), yttrium UiO-66, and a cerium MOF[5] as potential candidates for nanocasting.

Introduction

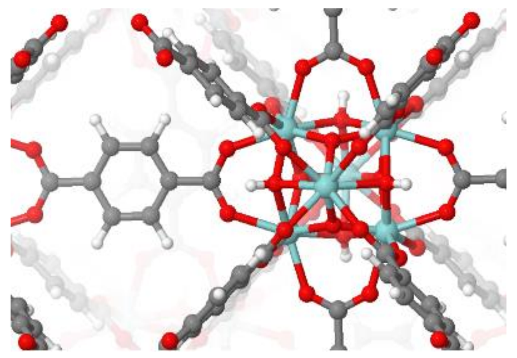


DUT-9[4]

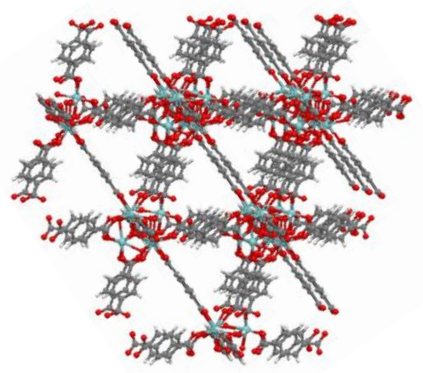
MOFs as catalysts

- ✓ High surface area
- ✓ Single-sites (improve selectivity)
- ✓ Post synthetic metalation
- ✓ Nodes with multiple metals
- ✗ Linkers are not stable over 350 °C[6]

Color code: red: O; black or grey: C; white: H; blue; green: Ni



UiO-66 close view[7]



UiO-66 general view[7]

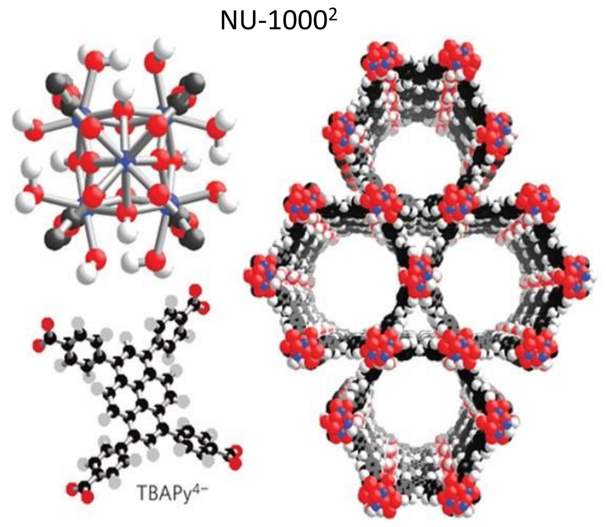
Nanocasting

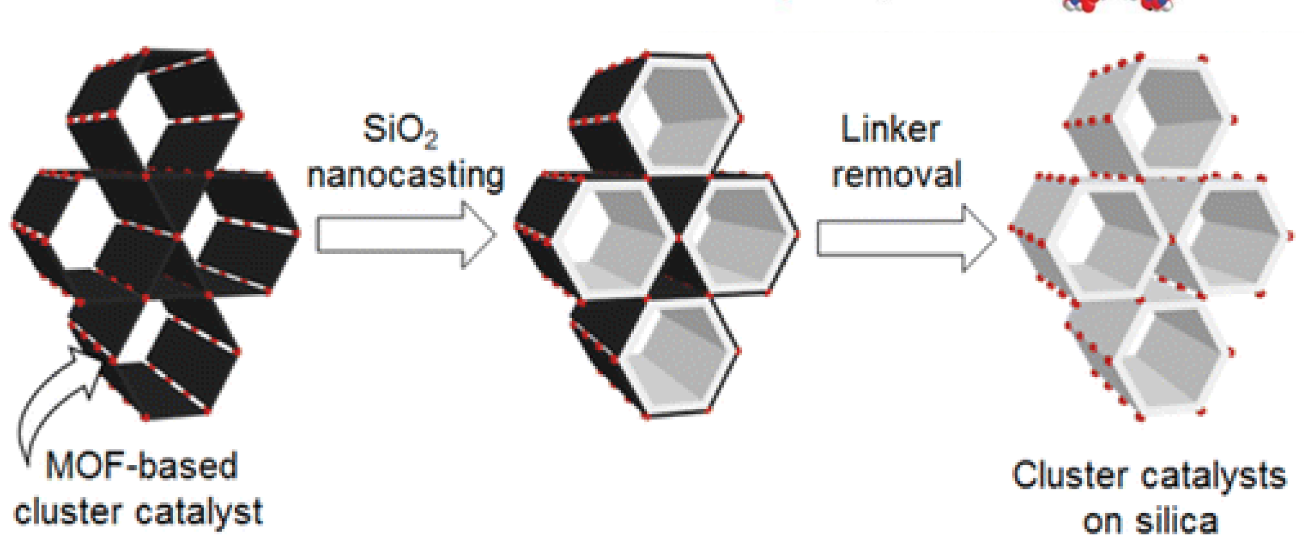
- ✓ Improve thermal stability
- ❑ TMOS mixture infiltration (24 h)
- ❑ HCl vapor exposure (24 h)
- ❑ Heat treatment (60 °C, 24 h)

Linker removal

- ❑ 500 °C (1 h, 2 °C ramp rate)

NU-1000[2]



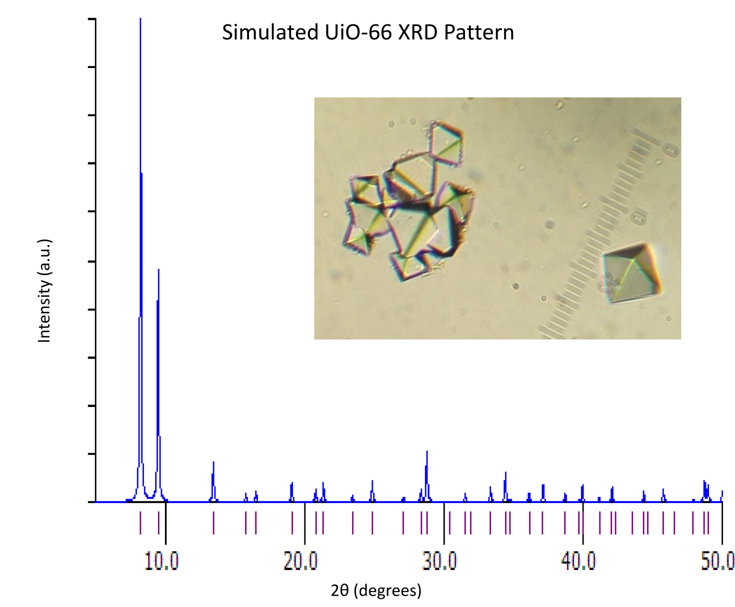


NU-1000 Nanocast using tetramethylorthosilicate (TMOS) mixture as casting fluid.[1]

MOF Synthesis

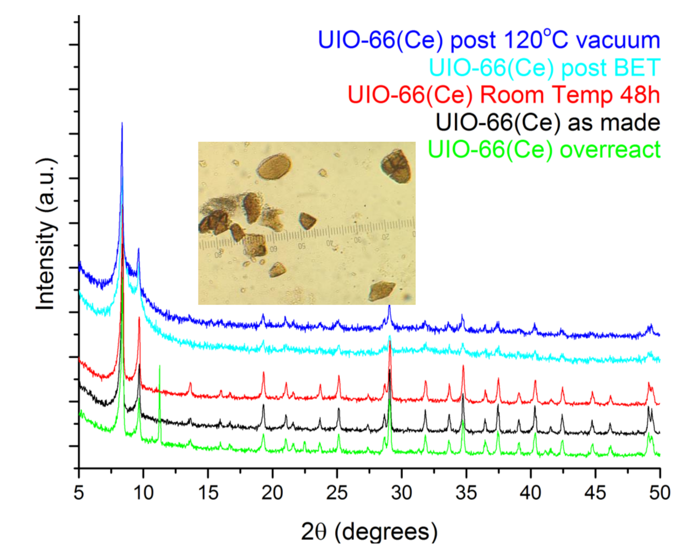
UiO-66 (Zr)[8]

- ❑ Terephtalic acid (BDC) in *N,N*-dimethylformamide (DMF)
- ❑ $ZrOCl_2 \bullet 8H_2O$ in water
- ❑ Mix the above solutions
- ❑ Heated at 130 °C for 3 days
- ❑ Wash twice with DMF, then twice with acetone and air dry



UiO-66 (Ce)[5]

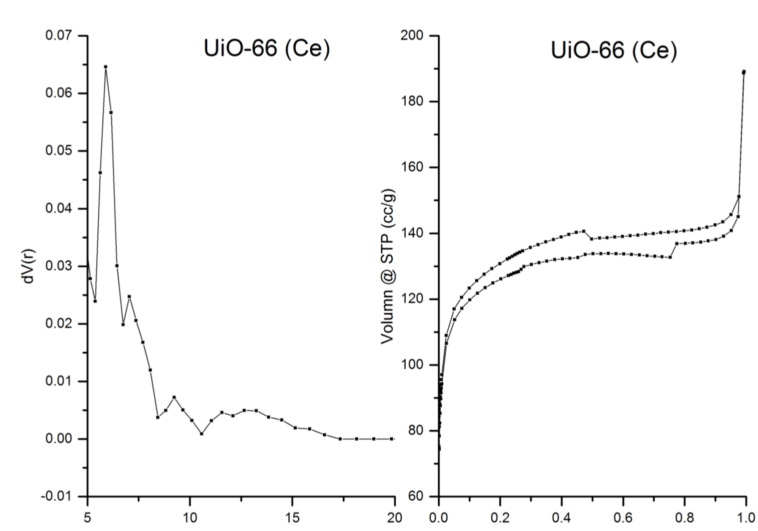
- ❑ Terephtalic acid (BDC) in *N,N*-dimethylformamide (DMF)
- ❑ Ammonium cerium (IV) nitrate in water
- ❑ Mix the above solutions
- ❑ Heated at 100 °C for 15 min
- ❑ Wash, dry at 70 °C



Potential Causes

- ❑ Extra DMF solvent left in pores during activation

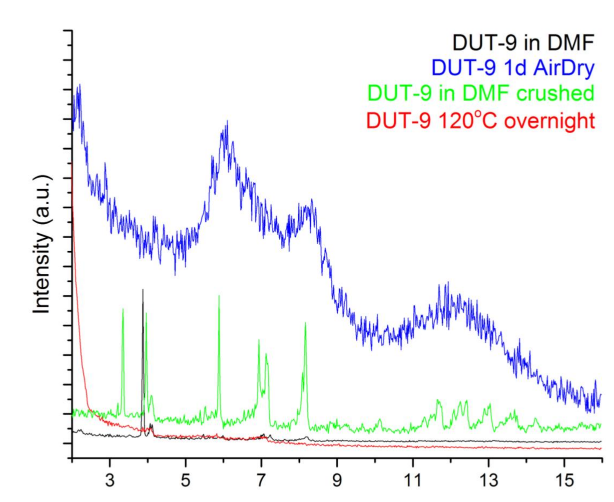
- ✗ Peak broadening after activation at 120 °C or 130 °C

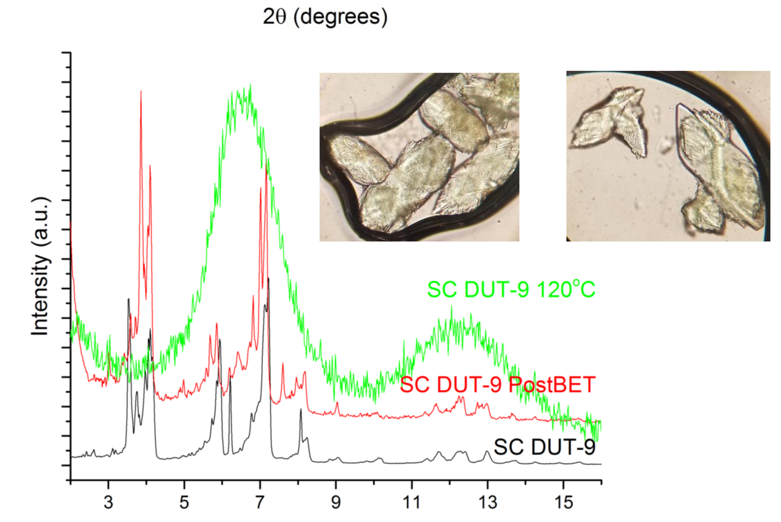


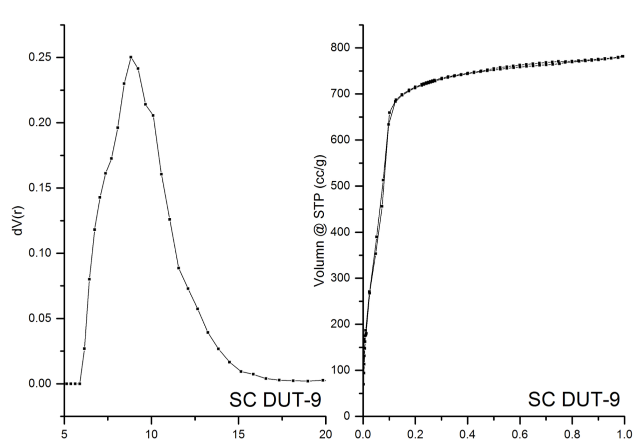
- ✗ Surface area is small (384 m^2/g) comparing to ref. value ~1100 m^2g.[5]

DUT-9 (Ni)[4]

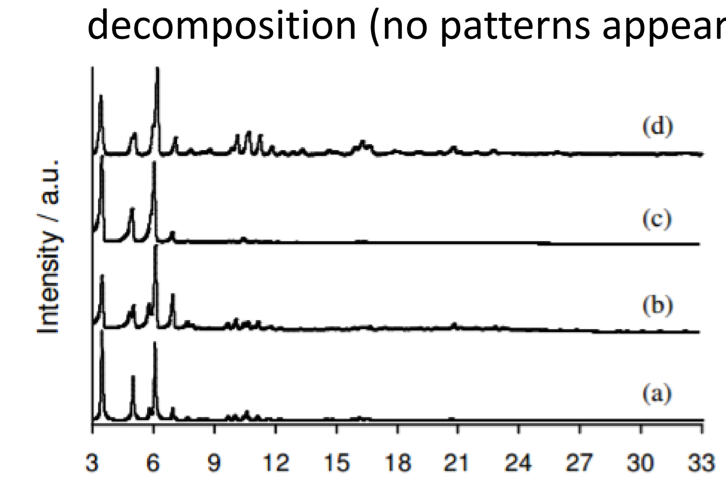
- ❑ H_3btb and $Ni(NO_3)_2 \bullet 6H_2O$ in *N,N*-diethylformamide (DEF)
- ❑ Heated at 120 °C for 20 h
- ❑ Wash twice with DEF
- ❑ Supercritical drying





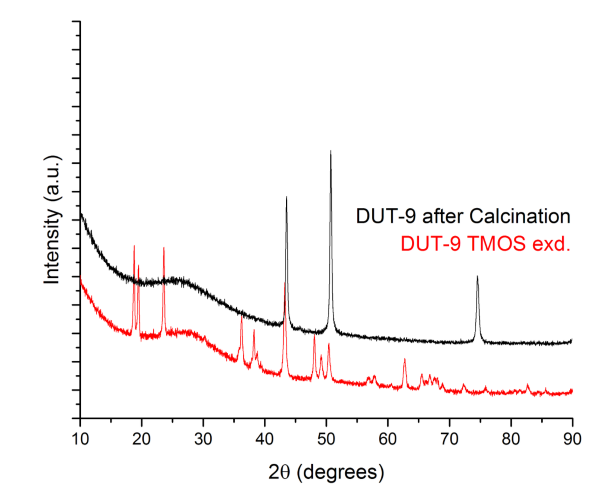


- √ Supercritical drying works better than air drying
- √ DUT-9 XRD pattern is better after crushing
- ✗ Activation at high vacuum introduces more peaks
- ✗ Drying sample at 120 °C leads to decomposition (no patterns appear)

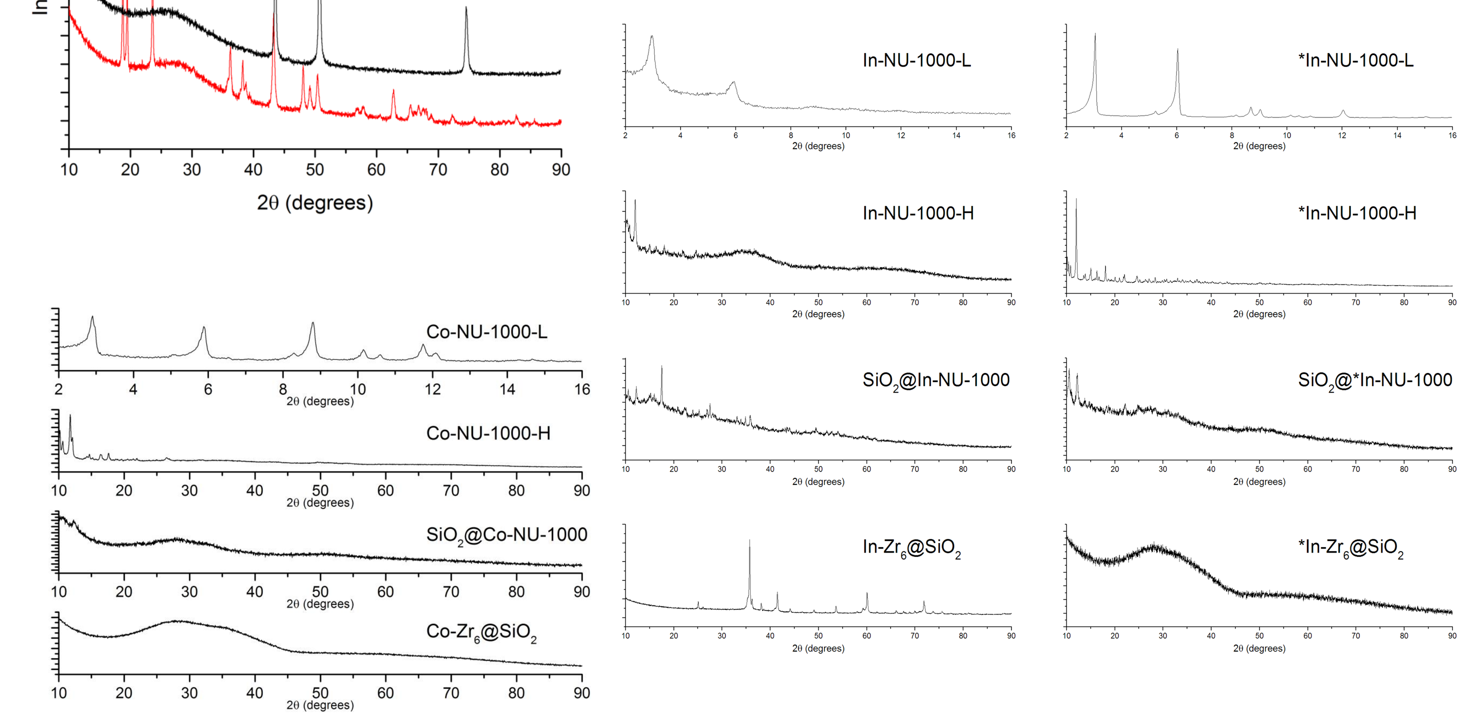


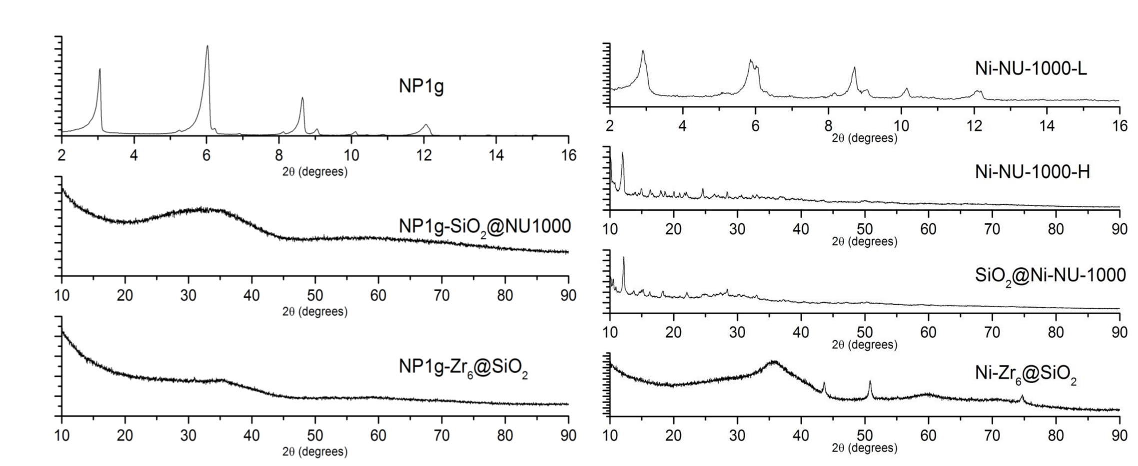
XRD patterns: (a) theoretical pattern; (b) as made; (c) supercritically dried (SC); (d) SC and additionally activated in vacuum at 120 °C[4]

Nanocasting



- √ Infiltration did not lead to nickel oxide aggregation
- ✗ Peaks at 2θ ≈ 43°, 51°, 75° indicated aggregation of nickel oxide from DUT-9
- ✗ Lose porous structure once dried inappropriately





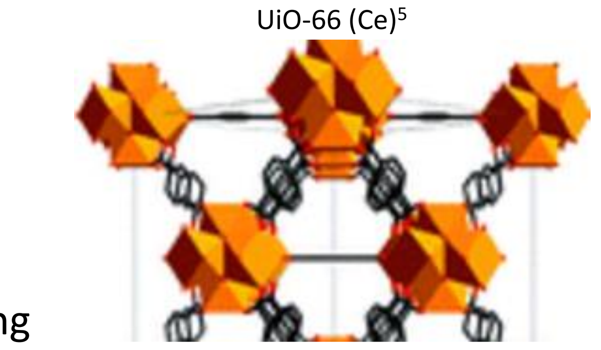
- ✓ NU-1000 & Co-NU-1000 Nanocast without cobalt oxide aggregation after calcination
- ✗ Metal oxide aggregation observed in Ni-, In-NU-1000

Conclusions and Future Plan

Conclusions

- ✓ Synthesized DUT-9, UiO-66 (Zr), UiO-66 (Ce)
- ✓ Successfully nanocast NU-1000 & Co-NU-1000

UiO-66 (Ce)[5]



Future Plan

- ❑ Develop method to dry DUT-9 during nanocasting
- ❑ Modify nanocasting procedure for unsuccessful samples
- ❑ Prolong acetone washing period for UiO-66 (Ce) and nanocast UiO-66 (Ce)
- ❑ Modify MOFs with other linkers to modify pore size
- ❑ Find MOFs with multiple metal clusters in the node
  - ❑ Different metal nodes → Different catalytic properties
  - ❑ Larger number of metals per node → Higher efficiency
- ❑ Send modified sample to other groups for catalytic activity test

References and Acknowledgements

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